

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 210/00, 4/642	A1	(11) International Publication Number: WO 96/34023 (43) International Publication Date: 31 October 1996 (31.10.96)
(21) International Application Number: PCT/FI96/00222 (22) International Filing Date: 23 April 1996 (23.04.96) (30) Priority Data: 951970 25 April 1995 (25.04.95) FI (71) Applicant (for all designated States except US): BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): AALTONEN, Päivi [FI/FI]; Kuhatiehahde 1 B 11, FIN-02170 Espoo (FI). LÖFGREN, Barbro [FI/FI]; Niittyrinta 17 B, FIN-00930 Helsinki (FI). SEPPÄLÄ, Jukka [FI/FI]; Rantakiventie 18 as. 6, FIN-00960 Helsinki (FI). (74) Agent: NESTE OY; Patent Services, P.O. Box 310, FIN-06101 Porvoo (FI).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>In English translation (filed in Finnish).</i>
(54) Title: A METHOD FOR MANUFACTURING OLEFIN COPOLYMERS CONTAINING FUNCTIONAL GROUPS AND POLYMERS OBTAINED BY THE METHOD (57) Abstract A method for the manufacture of olefin copolymers containing functional groups by polymerizing a 2-5 carbon atom olefin with a monomer containing a functional group, at an elevated temperature in the presence of a catalyst which polymerizes the olefin, by using metallocene catalysts.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LJ	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

A method for manufacturing olefin copolymers containing functional groups and polymers obtained by the method

- 5 The invention relates to a method for the polymerization of olefins and monomers ining functional groups.

The linking of monomers which contain functional groups to a hydrocarbon polymer chain signifies the creating of a usable method for the modification of the chemical and physical
10 properties of olefins. By using monomers containing functional groups it is possible to improve properties such as adhesion, dyeability, printability and permeability. Furthermore, a functional group provides a possibility for graft copolymerization and thereby for uses such as compatibilization of blends containing polyolefins.

- 15 The Ziegler-Natta catalyst system is commonly used in the polymerization and copolymerization of olefins, but one of the major limitations of these conventional catalysts is that they are not suited for use in conjunction with monomers containing polar monomers. Ziegler-Natta catalysts rather form a complex with the electron pair of a heteroatom, and thus in polymerization they rapidly deactivate the active centers by forming a stable
20 complex with the functional group. In other words, the catalysts are poisoned in the presence of functional groups.

Therefore the conventional method for the manufacture of olefins containing functional groups has been high-pressure polymerization by using free radical catalysts. In polymeri-
25 zations of this type, it is possible to link highly different groups to olefins. The high-pressure process typically yields products having a low density.

An example which can be given of high-pressure processes for the manufacture of olefin polymers containing functional groups is EP 092070, in which the catalyst is peroxide and
30 the polymerization is carried out at a pressure of 350-5000 bar. Patent applications DE 3227331 and DE 1185816 also relate to free radical polymerization at high pressure and temperature.

The more a polar compound resembles alpha-olefin, the greater its potential to be polymerized by the same active centers as olefins. In practice this non-desirable mutual interaction can be minimized by certain methods, such as (a) by isolating the double bond from the heteroatoms by means of a longer hydrocarbon chain; (b) by adding a steric
5 barrier around the heteroatom; (c) by decreasing the electron donor character of the heteroatom, for example, by linking to it or in its vicinity a group which attracts electrons; (d) by selecting catalyst components which are inert to functional groups; (e) by precomplexing the functional monomer by using a Lewis acid; or (f) by using a polar solvent which becomes polarized with the active center but allows the polymerization of
10 the vinyl monomer.

If deactivation can be successfully prevented by one or several of the above-mentioned methods, the copolymerization of functional monomers will become more popular than it is today.

15

US patent publication 5.286.800 discloses the polymerization of comonomers containing functional groups with alpha-olefins. In these polymerizations there are used borane monomers which are converted, by reactions after the polymerization step, into poly-olefins which contain functional groups.

20

In Japanese patent publication 61 72 447, the comonomer used is 10-undecen-1-ol which has been pretreated with tri-isobutyl aluminum for 3 hours at room temperature before polymerization.

25 An object of the present invention is to provide a novel method for the manufacture of copolymers of olefins and monomers containing functional groups. Furthermore, one object of the invention is a method in which the catalyst system has in the presence of a polar group as high an activity as possible. One object of the invention is also to provide a method for the copolymerization of olefins in which the copolymerization with a polar
30 comonomer takes place in one step, without any pretreatment or after-modification. One further object according to the invention is the manufacture of functional polyolefins in which the molar masses remain relatively high and the molar mass distributions are wide.

According to the invention it has been observed that, if metallocene catalysts are used, it is, surprisingly, possible to polymerize olefins and monomers containing functional groups in one step and without any after-treatment.

- 5 Thus the method according to the invention for the manufacture of olefin copolymers containing functional groups by polymerizing an olefin containing 2-5 carbon atoms with a monomer containing a functional group, at an elevated temperature and in the presence of a catalyst which polymerizes the olefin, is characterized in that the catalyst used is a metallocene catalyst.

10

The olefin used in the manufacture of copolymers according to the invention consists of olefins containing 2-6 carbon atoms. Preferably, ethylene or propylene is used, but olefins having a longer carbon chain, such as 1-butene, pentene and 1-hexene, can be used just as well.

15

- The catalyst used is a metallocene-type catalyst. The metallocene may be a metallocene of any type. Thus, suitable metallocene compounds are compounds having the formula $(Cp)_mR_nMR'_oX_p$, where Cp is an unsubstituted or substituted and/or fused homo- or heterocyclopentadienyl, R is a group containing 1-4 carbon atoms which serves as a link
20 between two Cp rings, M is a transition metal belonging to group 4A, 5A or 6A (Hubbard), R' is a C_1 - C_2 hydrocarbyl or a hydrocarboxy group, and X is a halogen, m being 1-3, n being 0 or p being 0-3, and the sum $n+o+p$ corresponding to the state of oxidation of the transition metal M. The transition metal is preferably zirconium or hafnium, most preferably zirconium. Examples of suitable metallocene compounds include, among
25 others, bis(n-butylcyclopentadienyl) zirconium dichloride, 1,2-ethylene-bis(indenyl) zirconium dichloride, and 1,2-ethylene-bis(indenyl) hafnium dichloride.

- The polymerization activity of the catalyst can also be enhanced using activators such as alumoxane. One method is to add the alumoxane to the metallocene compound before,
30 simultaneously with, or after the metallocene. Another method is to introduce the activator directly into the polymerization reactor.

Suitable activators include alumoxane compounds having the formula $R-(Al(R)-O)_n-AlR_2$

or $(-Al(R)-O-)_m$, where n is 1-40, m is 3-40, and R is a C_1-C_8 alkyl group. Preferably R is a methyl group.

The support used may be any porous or inert support, such as silica or alumina or
5 mixtures thereof.

The polymerization can be carried out by any method, for example by slurry polymerization or gas phase polymerization. Thus the polymerization may be carried out, for example, at a temperature of 60-100 °C and under a pressure of 1-100 bar. The partial pressure of
10 olefin in the reactor may vary within a range of 1-3 bar and the amount of comonomer within a range of 0.5-10 mmol.

The invention is described below in greater detail with reference to the accompanying
examples.

15

Materials

Bis(*n*-butylcyclopentadienyl) zirconium dichloride, 1,2-ethylene-bis(indenyl) zirconium
20 dichloride, 1,2-ethylene-bis(indenyl) hafnium dichloride and methyl alumoxane (MAO) were all of a commercial grade and were not purified separately. The polymerization-grade ethylene and propylene, and the *n*-heptane and toluene serving as the medium were purified by feeding them via a column series to remove any residual moisture and oxygen. The comonomers 2-methyl-3-butenol and 5-hexen-1-ol were of a commercial grade and
25 they were purified by drying and nitrogenation.

Polymerization

Ethylene copolymerizations were carried out in an autoclave of 0.5 dm³ at temperatures
30 of both 60 °C and 80 °C for 40 minutes, the reaction medium used being *n*-heptane.

The medium *n*-heptane (350 cm³) was introduced into a vacuumized and nitrogenated reactor equipped with a stirrer. The rotation velocity of the stirrer was all the time 400

rotations per minute. The comonomer was added in one batch under nitrogenation, and the cocatalyst (MAO) (Al/M 4000 mol/mol, where M = Zr, Hf) was added at the beginning of the polymerization by using a pump. After the polymerization temperature had been reached, ethylene was fed into the reactor. Ethylene consumption was monitored
5 by means of a mass flow controller. After equilibrium had been reached, polymerization was started by pumping the catalyst into the reactor. The partial pressure of ethylene or propylene was maintained constant (2.5 bar ethylene pressure) by means of an electronic pressure controller and a solenoid valve, and the reactor temperature was maintained constant. The conversion was maintained low in order that it could be assumed that the
10 conversion in the reactor was constant. At 40 minutes, reactor pressure was released and the polymer product was washed with a solution of ethanol and hydrochloric acid and was dried.

The compositions of the copolymers of ethylene and functional monomers were determined by using a JEOL NMR spectrometer. The melting points and enthalpies were
15 determined from the peak of the DSC curve by using a Perkin Elmer DSC-7 instrument. The DSC measurements were carried out by reheating the sample to 180 °C at heating rates of 2 and 10 °C/min.

20 The molar masses and the molar mass distributions were measured using a Waters type ALC/GPC 150 instrument in which there had been installed 3 TOSOH mixed-bed columns in which the polystyrene barrier limit was 4×10^8 at a temperature of 135 °C. The solvent used was 1,2,4-trichlorobenzene having a flow rate of 1.0 ml/min.

25 Examples

Ethylene was copolymerized with various comonomers containing functional groups. The functional monomers used were 2-methyl-3-buten-2-ol and 5-hexen-1-ol. The catalyst used was a bis(n-butyldicyclopentadienyl) zirconium dichloride/MAO combination. The
30 polymerization conditions and the properties of the product are shown in Table 1.

Table 1

Example	Comonomer	Comonomer amount mmol	Activity kg/g cat.h	Molecular weight $M_w \times 10^{-3}$	M_w/M_n	T_m
1		-	26.1	222	3.4	136.7
2	2-methyl-3-buten-2-ol	1	22.3	150	3.7	137.2
3	"	2	16.2	183	3.1	136.0
4	"	3	10.6	177	3.4	134.2
5	"	4	8.3	183	3.1	135.6
6	"	5	6.1	161	3.8	135.9
7	"	6	5.2	172	3.7	134.7
8	5-hexen-1-ol	1	13.0	158	3.4	134.2
9	"	2	9.0	130	3.1	134.8
10	"	3	6.5	147	4.2	132.8
11	"	4	5.6	161	6.0	131.9

Examples 12-28

Propylene copolymerizations were carried out by the same procedure as the ethylene copolymerizations, except that the medium was used in an amount of 300 cm³, the polymerization time was 60 minutes and the polymerization temperatures were 30 °C and 60 °C, and the propylene overpressure was 3.0 bar. Both 1,2-ethylene-bis(indenyl) zirconium dichloride and 1,2-ethylene-bis(indenyl) hafnium dichloride were used as catalysts. The results are shown in Tables 2 and 3.

Table 2 Catalyst 1,2-ethylene-bis(indenyl) zirconium dichloride

Example	Monomer	Monomer amount mmol	Yield g	M_w	M_n	M_w/M_n
12	5-hexenol	1.01	18.7	30500	14800	2.06
13	"	1.69	8.4	27000	13500	2.00
14	"	2.96	5.4	25200	12100	2.08
15	"	3.38	2.6	22100	10200	2.17
15	"	3.97	1.7	21200	9940	2.13
16	2-methyl- 2-buten-1-ol	0.96	41.0	32200	16100	2.00
17	"	1.91	20.4	30600	15400	1.99
18	"	2.97	12.6	29900	15300	1.95
19	"	3.83	9.6	30300	15500	1.95
20	"	5.74	3.2	31400	15900	1.97

15

Table 3 Catalyst 1,2-ethylene-bis(indenyl) hafnium dichloride

Example	Monomer	Monomer amount mmol	Yield g	M_w	M_n	M_w/M_n
21	5-hexenol	0.50	3.4	71100	34700	2.05
22	"	1.00	0.6	42600	20500	2.08
23	"	1.50	0.5	36700	18300	2.01
24	2-methyl- 2-buten-1-ol	1.00	10.5	94300	45700	2.06
25	"	2.01	5.6	91700	44000	2.08
26	"	3.01	3.7	86000	40200	2.14
27	"	4.02	1.1	73600	33700	2.18
28	"	5.02	0.2	51700	23600	2.19

Claims

1. A method for the manufacture of olefin copolymers containing functional groups by polymerizing a 2-5 carbon atom olefin with a monomer containing functional groups, at
5 an elevated temperature and in the presence of a catalyst which polymerizes the olefin, characterized in that the catalyst used is a metallocene catalyst.
2. A method according to Claim 1, characterized in that the metallocene is selected from bis(n-butylcyclopentadienyl) zirconium dichloride, 1,2-ethylene-bis(indenyl)
10 zirconium dichloride and 1,2-ethylene-bis(indenyl) hafnium dichloride.
3. A method according to Claim 1 or 2, characterized in that the polymerization is carried out using methyl alumoxane (MAO) as an activator.
- 15 4. A method according to any of the above claims, characterized in that the functional monomer is selected from 2-methyl-3-buten-2-ol, 2-methyl-3-buten-1-ol, 3-methyl-3-buten-1-ol and 5-hexen-1-ol.
5. A method according to any of the above claims, characterized in that the olefin is
20 selected from ethylene and propylene.
6. Olefin copolymers containing functional groups, which copolymers have been prepared by a method according to any of the above claims.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 96/00222

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 210/00, C08F 4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0092070 A2 (BASF AKTIENGESELLSCHAFT), 26 October 1983 (26.10.83) --	1-6
A	EP 0552945 A2 (MITSUI PETROCHEMICAL INDUSTRIES, LTD), 28 July 1993 (28.07.93) -- -----	1-6

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another claim or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

23 July 1996

Date of mailing of the international search report

24 -07- 1996

Name and mailing address of the ISA/
Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Jack Hedlund
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/07/96

International application No.

PCT/FI 96/00222

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP-A2-	0092070	26/10/83	DE-A, A-	3212748	13/10/83
<hr/>					
EP-A2-	0552945	28/07/93	CA-A-	2087905	24/07/93
			CA-A-	2087916	24/07/93
			EP-A, A-	0552946	28/07/93
			JP-A-	5262827	12/10/93
			JP-A-	6228228	16/08/94
			KR-B-	9514846	16/12/95
			KR-B-	9514847	16/12/95
			US-A-	5292845	08/03/94
			JP-A-	6263821	20/09/94
<hr/>					